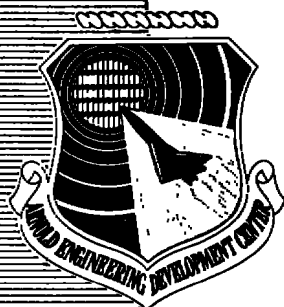C·2

ON THE EFFECTIVENESS OF ANODIZED ALUMINUM CRYO-PANELS TO PUMP H_2

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September 1979

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FOR THE COMMANDER

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FOREWORD

The work reported herein was sponsored by the Arnold Engineering Development Center (AEDC), Directorate of Test Engineering, Research Division (DOTR), under Program Element 65807F. The results were obtained by ARO, Inc., AEDC Division (a Sverdrup Corporation Company), operating contractor for the AEDC, AFSC, Arnold Air Force Station, Tennessee under ARO Project No. P32K-13, Part 4, Cryopumping Development for Contamination Studies. The Air Force Project Manager was Captain K. H. Leners.

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SUMMARY

Studies of the pumping of H_2 by anodized aluminum cryopanels have indi-
cated that they offer considerable potential for space chamber application.
The aluminum foam cryopumps adsorbed sufficient H_2 when cooled to $28^{\circ}K$ to
serve as practical cryosorption pumps. Future studies should consider opti-
mization of foam geometry (thickness of foam and spacing of cooling coils) and
contamination effects from substances such as diffusion pump oil and the liquid
fuels of monopropellant and bipropellant engines.

CONTENTS

NOMENCLATURE

A	area, cm^2
a	constant
C	capacity, torr-ℓ
k	volumetric flow rate, ℓ/sec
M	molecular weight
m	constant
P	pressure, torr
Q	mass flow rate (20°C), torr-ℓ/sec
S	pumping speed, ℓ/sec
T	temperature, °K
V	volume, ℓ

1.0 INTRODUCTION

The vacuum chambers at AEDC have been used successfully for simulating exoatmospheric conditions for rocket motor firings. In these tests, extensive use of cryopumping and cryosorption is required in order to trap the exhaust gases and prevent them from rebounding into the test volume. In order to reproduce free space conditions faithfully, all gas species must be captured as they reach the chamber walls. Of all the gas species present in both liquid and solid propellant rockets, hydrogen is the most difficult to capture.

Hydrogen may be cryopumped directly if LHe-cooled panels are available since it has a vapor pressure of about 3×10^{-7} torr at $4.2^{\circ}K$. The vapor pressure of H_2 is 5×10^{-5} torr at $5.2^{\circ}K$. This is the critical temperature of LHe and thus represents the upper limit for LHe cooling (Ref. 1). In many instances, however, LHe is not available, or is not economically feasible to use, in the quantities required to pump large systems. In the past decade it has been shown (Refs. 2 to 7) that hydrogen can be successfully pumped by sorption on cryodeposited frost formed by condensing certain gases such as carbon dioxide (CO_2), water (H_2O) vapor, etc., on surfaces at temperatures between 10 and $20^{\circ}K$.

However, this technique has several limitations in that there are difficulties in predepositing the cryofrost uniformly; it adds an additional heat load to the refrigeration equipment, and in cases where the test also includes cryogenically cooled sensors and optical surfaces the cryofrost is an unwanted contaminant.

There is therefore a continuing need for a method to remove H_2, which is more economical than LHe cryopumping and less troublesome to apply than the gaseous cryodeposited sorbents.

It has been reported by Kosherov et al. (Ref. 8) that H_2 is adsorbed on anodic oxidized aluminum cryosurfaces cooled to $77^{\circ}K$. Several general claims are made for the anodized aluminum cryopump. These include:

1) Excellent thermal conductivity between substrate and sorbent.

2) The sorbent is rugged and resists abrasion or physical damage.

3) The system is reusable after a simple bakeout.

4) A five-fold increase in the thickness of the oxide film resulted in an increase in the sorption capacity by a factor of 10 to 20.

While the amount of H_2 adsorbed at $77^{\circ}K$ is not enough to construct a practical pumping system, the data do suggest that sufficient quantities are adsorbed to warrant further investigation of this pumping technique at the colder temperatures where the capacity might increase significantly.

The experiments reported herein were conducted to evaluate the effectiveness of anodized aluminum panels to pump H_2.

2.0 APPARATUS

2.1 VACUUM CHAMBER

This work was performed in the 2- by 3-ft Research Ultrahigh Vacuum Chamber described in detail in Ref. 9 and shown in Fig. 1. After deducting the space taken by the cylindrical cryopump and the radiation shrouds, it has a free volume of 300 liters. The radiation baffles are vented to allow free passage of gas molecules, yet they are optically tight between the outer chamber walls and the cryosorption pump. The chamber is pumped by a 6-in. diffusion pump with an LN_2 cold trap. This system can be valved off with a 6-in. gate valve.

2.2 ANODIZED CRYOPUMP

The anodized cryopump consists of a 12-in. by 16-in. by 1/8-in. aluminum plate. On one side was welded a 1/2-in.-inside-diam tubulation. This tubulation carries the cold GHe from the refrigerators. A 2-in.-thick layer of expanded foam aluminum was bonded to the other side. The complete panel was anodized and is shown in Fig. 2.

Several bonding techniques were evaluated. The first consisted of an aluminum filled epoxy. The flat plate was abraded and an even coating of epoxy was applied to the surface. One side of the foam aluminum was sanded smooth and embedded in the epoxy. The panel was air cured for 48 hours. The bond was tested by shock cooling from room temperature to 77°K by immersion in LN_2. Signs of separation at the plate occurred after the first cooldown and the bond failed completely after the third cycle. The epoxy held securely to the foam.

A second attempt was made using a matrix of 1/4-in.-diam spots over the surface of the plate and the test was repeated. This test panel survived five cooldowns and the foam remained attached to the plate. However, when the plate was sectioned it was found that 60 percent of the bonds had failed. This would limit the heat transfer surface severely and was thus not considered acceptable.

A sample of the plate and foam was prepared for vacuum brazing. The sample was not successful since the foam material slumped during the heat cycle. It is felt that the material could be brazed, however, it would require an oven with a more sensitive heat controller. This also would be a serious problem in trying to fabricate large panels for a practical sized pumping system.

Several types of aluminum solders were evaluated. From these, the most successful bond was formed using the following technique.

1) The surface of the plate and the bond surface of the foam were cleaned with ARCAL Weld-O® preparation.[*] This is a commercial preparation of acids used to remove all grease and oxides from the aluminum.

2) The surface of the plate was coated with flux[**] and heated with an acetylene torch. A small quantity of ALU-SOL multicore® solder[***] was applied to the surface and brushed across with a stainless steel brush. This wetted the surface and effectively tinned the entire area.

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[*] Arcal Chemicals, Inc., 223 W. Hampton Ave., Seat Pleasant MD 20027.
[**] Eutector® Alutin 51B. Eutectic Corporation, 40-40 172 St., Flushing NY.
[***] 45D 814/84 Multicore Solders Ltd. Hemel Hempstead Herts, U.K.

3) ALU-SOL multicore solder, supplied in 16 swg gage wire was cut into 8-in. lengths and formed into flat coils approximately 1-in. in diameter. These coils were placed in a matrix on 1.5-in. centers

4) The plate and foam with the sandwiched solder wire was placed in an oven and heated to 300°C under an inert atmosphere of argon.

5) The oven was slowly cooled and the bonded panel was removed and washed with flux remover (Type 1002 Etectic*).

A panel produced using this technique withstood repeated heat shocks from room temperature to 77°K with no indication of bond failure. However, it became apparent during the subsequent anodizing process that some of the flux still remained embedded in the foam. This prototype panel was therefore not evaluated due to the contaminated anodized coating. It is felt that this bonding technique is feasible with a more thorough clean-up.

Two cryopanels were constructed by first anodizing the panels and the foam and then cementing the panels to the foam with a low temperature epoxy developed by NASA for LH_2 service.**

The bond survived repeated cooldowns to cryogenic temperatures. Thermocouples were attached to one of these panels and it was installed in the test chamber and evaluated for its ability to cryosorb hydrogen. The panel specifications are presented in Table 1.

Table 1 Sorption Pump Specifications

Material	Duocel Foam Aluminum® 6101 aluminum 6% density
Size	42-cm x 30-cm x 5-cm
Processing	Anodized – no seal – no dye
	60 minutes at 250 amps
	80°F, 15% H_2SO_4 solution
Bonding	Furane Epibond 123 with 9615-10 hardener (2:1)
	Air cure
Ratio of area/vol of foam	11.8 cm^2/cm^3
Effective surface area for sorption	7.4 x 10^4 cm^2
Area of pump envelope	1.98 x 10^3 cm^2

Energy Research and Generation, Inc., Lowell & 57th Sts., Oakland, CA.

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* Eutectic Corp. 40-40 172 St., Flushing, NY 11358.
** Furane Epibond 123 with 9615 hardener. 2:1.

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2.3 GAS ADDITION SYSTEMS

Associated with the chamber is a gas addition system. Gases may be metered into the chamber at various rates. This system uses a set of sintered steel leaks which have been calibrated in situ. Details of this system may be found in Ref. 5. The gas system enters the chamber and ends outside the shroud. Gas added thus has to diffuse through the open shroud before reaching the pump surface.

2.4 INSTRUMENTATION

Pressures in the vacuum chamber were monitored by an ionization gage connected to a tube which penetrated the shroud and thus sampled a gas flux similar to that "seen" by the pump surface. Temperatures of the gaseous He cooled panel were monitored with CuCn thermocouples. Inlet and outlet temperatures of the gaseous helium refrigerator were monitored with H_2 vapor pressure thermometers.

3.0 CALIBRATION

3.1 LEAKS

Each leak in the gas addition system was calibrated for hydrogen. The method consisted of monitoring the rate of pressure drop in the reservoir of known volume as the gas flowed from this volume, through the leak, and into the vacuum chamber. Pressures in the reservoir were in the 5- to 800-mm range and were recorded by instruments calibrated against mercury manometer standards. Full details of this procedure and analysis of the method are included in Ref. 5.

3.2 GAGE CALIBRATION

The ion gage was calibrated in situ. The method used was to bleed H_2 into the chamber at various known rates through the calibrated leak system and to record both the rate of rise with the diffusion pump valved off and the equilibrium pressure with the gate valve open. This method is outlined in detail in Ref. 5. The data produced can be used to determine both the calibration constant for the ion gage and the pumping speed of the diffusion pump. A thermal transpiration factor was used to correct the ion gage calibration constant when the liner was cooled to $77^\circ K$.

4.0 PROCEDURE

The chamber was pumped to its base pressure of 8×10^{-7} torr and the ion gage was calibrated for H_2. The cryogenic systems were then turned on and the shroud was cooled to $77^\circ K$ with LN_2 and the aluminum cryopump was cooled by the gaseous helium refrigerator. With all systems cold the base pressure dropped to low 10^{-8} torr. At this point the diffusion pump was valved off. The chamber pressure registered a very slow rate of rise which was determined to be due to a small He leak (1.2×10^{-7} torr-ℓ/sec). This is negligible when compared to the addition rate of the H_2 test gas and no attempt was made to eliminate it.

Hydrogen was admitted via the calibrated leak system and the resulting pressure rise on the ion gage was noted. This process was repeated with various H_2 addition rates.

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When the chamber pressure had risen to mid 10^{-5} torr all H_2 addition was stopped and the gate valve to the diffusion pump was opened. The refrigeration to the aluminum cryopump was reduced and the panel was allowed to warm up to 100°K.

After the H_2 had been removed by the diffusion pump, the gate valve was closed and the procedure repeated with the aluminum cryopump recooled. The identical gas addition procedure was followed in order to determine if the cryopump had been completely rejuvenated by the limited warmup to 100°K.

5.0 RESULTS

The initial H_2 gas addition was made through the 10^{-5} ℓ/sec leak at a rate of 1.8×10^{-4} torr-ℓ/sec and was pumped by the cryopanel with 100 percent efficiency. The gas addition rates were therefore increased and measurements made to determine both the pumping speed of the sorption pump and an adsorption isotherm for the anodic coating.

For a closed system the rate of gas bled into the vacuum chamber Q can be equated to the amount removed by the pump plus the rate of pressure rise in the chamber.

$$Q = \dot{P}_c V + S P_c$$

where
$\quad Q = P_f k$
$\quad P_f = $ forepressure on the gas leak (torr)
$\quad k = $ size of the leak (ℓ/sec)
$\quad \dot{P}_c = $ rate of pressure rise (torr/sec)
$\quad V = $ volume of the chamber (ℓ)
$\quad P_c = $ pressure in the chamber (torr)
$\quad S = $ pumping speed of pump (ℓ/sec)

Using these relationships and the data from the first set of pumping experiments, for a gas addition rate of 0.19 torr-ℓ/sec the resulting chamber pressure was 4.5×10^{-6} torr and was slowly rising at a rate of 1.2×10^{-8} torr/sec (Fig. 3). Solving for the pumping speed S yields

$$S = 4.2 \times 10^4 \text{ ℓ/sec}$$

A theoretical maximum pumping speed can be calculated for the cooled foam by considering the theoretical strike rate of the H_2 gas and the area of the outer surface (envelope)

$$S_{theor} = 3.65 \ A \sqrt{\frac{T}{M}} \text{ (ℓ/sec)}$$

where
$\quad A = $ envelope surface area (cm^2)
$\quad T = $ temperature of gas ($^{\circ}$K)
$\quad M = $ molecular weight of gas

The envelope surface area of the 30-cm by 42-cm by 5.0-cm foam is 1980 cm^3. Since the chamber has a 77°K liner then

$$S_{theor} = 4.5 \times 10^4 \; \ell/sec$$

As can be readily seen, the pump is adsorbing H_2 with an almost 100 percent efficiency. The slow pressure rise indicates that the gas is being added to the system slightly faster than the pump can adsorb it.

At this point in the H_2 gas addition sequence 35.3 torr-ℓ of H_2 had been adsorbed by the pump. Beyond this point the residual equilibrium partial pressure of H_2 was observed after each gas addition and an isotherm determined as shown in Fig. 4. The actual temperature of the foam is open to some question. The thermocouple was attached by soldering it to a copper washer and then clamping the washer to the foam with a sheet metal screw. The recorded temperature of $45^\circ K$ was considerably warmer than the backing plate which was cooled to $28^\circ K$. The thermocouples on the plate and the inlet and return cryogenic lines all matched within 1 or 2 degrees the temperatures recorded by the supply and return vapor pressure thermometers of the cryostat. In a subsequent cooldown an indium disc was placed between the thermocouple washer and the foam. With this modification the thermocouple on the foam matched the readings from the one on the plate. It is therefore suggested that the isotherm presented in Fig. 4 is for the foam at $28^\circ K$, the $45^\circ K$ temperature being in error due to poor thermal contact.

The shape of the isotherm suggests a complex sorption system. For very small concentrations, gases usually adsorb according to Henry's law (Ref. 10),

$$C = aP^m$$

where $m = 1$ for non-metals.

The data for the pressure range 10^{-8} to 10^{-6} are plotted in Fig. 5 and are seen to agree very well with this prediction. However, at the higher pressures the form of the isotherm is similar to that suggested by Brunauer (Ref. 11) for sorbents with small capillaries or narrow-necked micropores. This is consistent with the structure of the anodized coating.

Figure 6 shows enlarged views of the anodized surface. These photographs taken under a scanning electron microscope further confirm the small crevices in the surface.

In order to compare this pumping technique with that of CO_2 cryosorption then, the capacities can be considered as a function of the geometric envelope of the cryopanel. For CO_2 at $20^\circ K$ with a precoat of 0.5 torr-ℓ/cm^2 of CO_2, the capacity (1×10^{-5} torr) was 7.5×10^{-3} torr-ℓ/cm^2 of H_2 (Ref. 5). The anodized panel adsorbed 0.1 torr-ℓ/cm^2, thus indicating a significant improvement over precoated CO_2 for a comparable area of cryopumping surface.
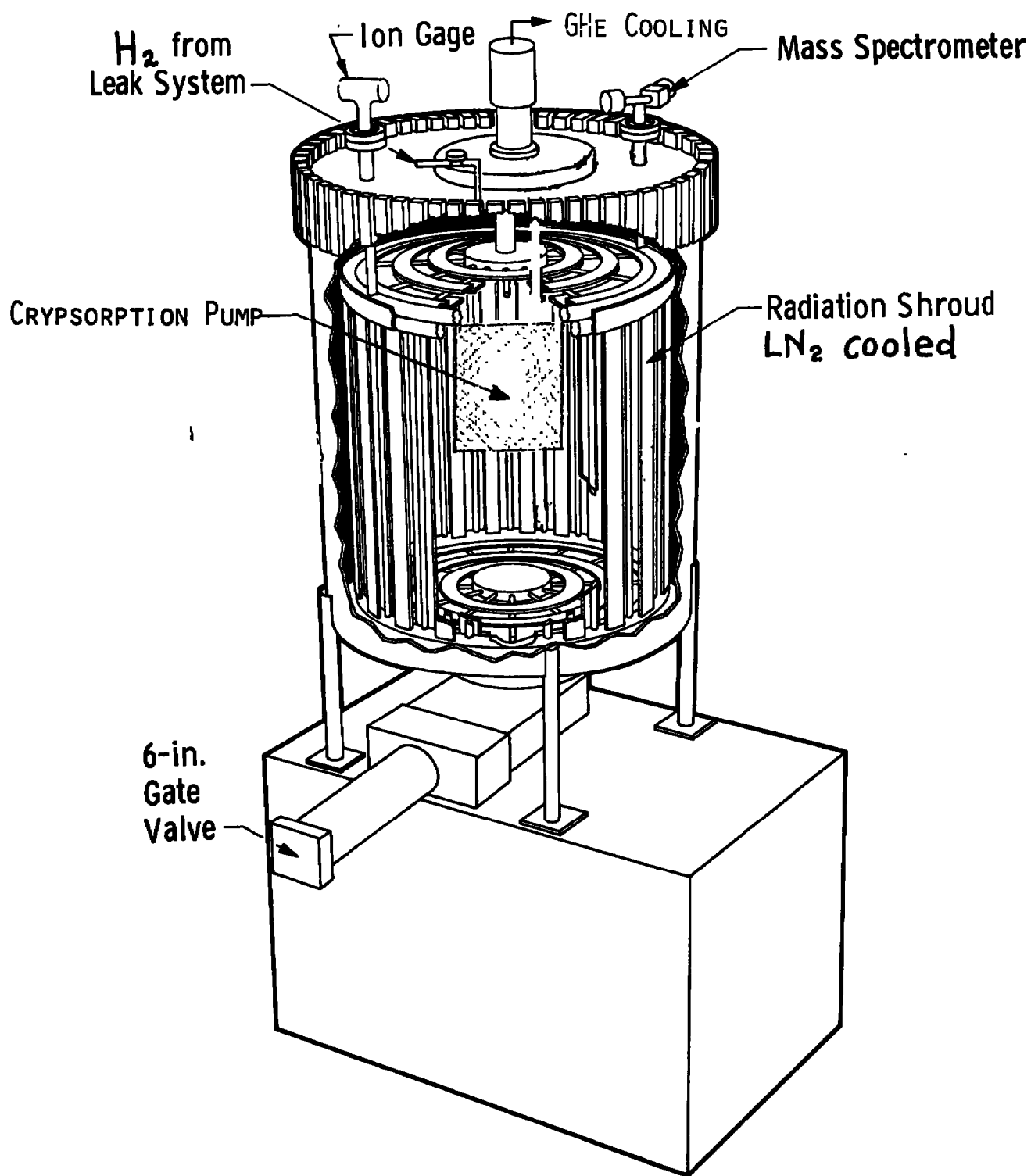
6.0 CONCLUSIONS

The anodic coating on the aluminum foam adsorbs sufficient H_2 at temperatures of $28^\circ K$ to construct a practical pumping system. The prototype panel evaluated in this project was successfully rejuvenated by warming to $100^\circ K$ and then recooling. The epoxy bonding survived the cooldown and warmup cycles with no obvious signs of separation and thus can be considered a satisfactory bonding technique.

Several factors still need to be evaluated before this technique can be recommended for full scale implementation. The most important is the ability of the panel to survive contamination and cleaning. The prime contaminants to consider are diffusion pump oils and liquid rocket fuels (hydrazine and MMH).

Further studies of these effects are recommended.

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H₂ from Leak System

Ion Gage

G̃He COOLING

Mass Spectrometer

CRYPSORPTION PUMP

Radiation Shroud LN₂ cooled

6-in. Gate Valve

Fig. 1 Schematic of Pumping Research Chamber

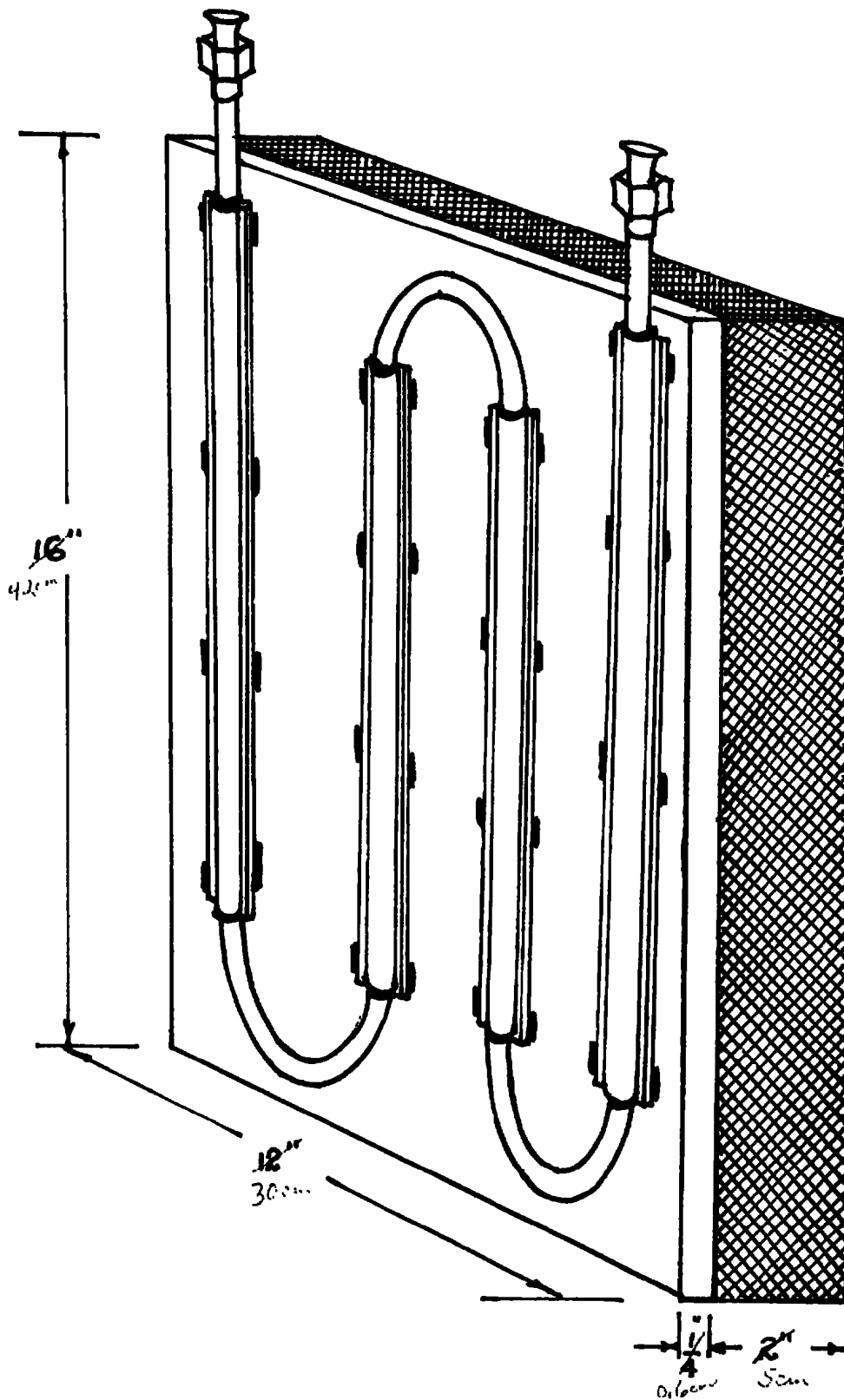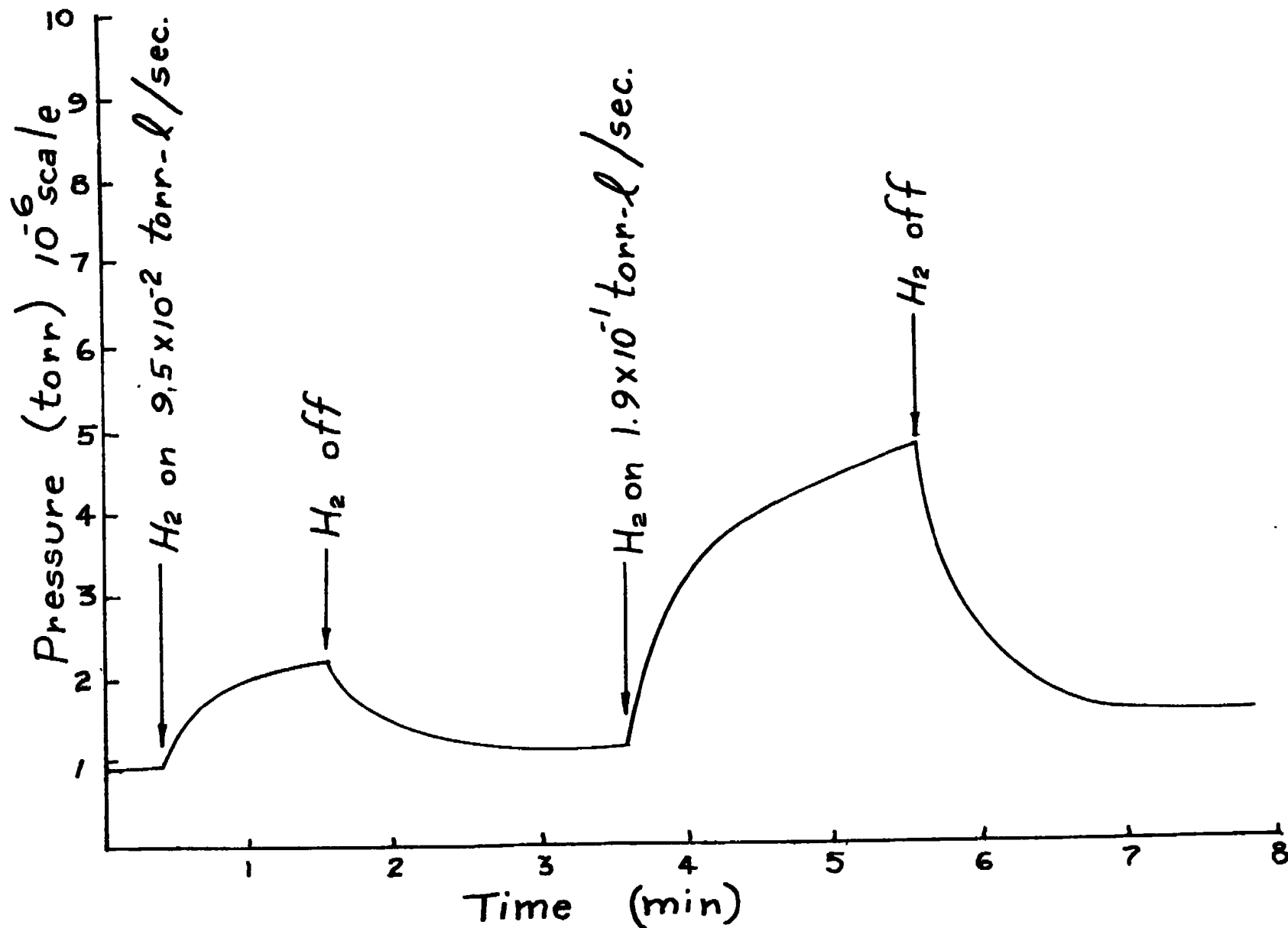# Anodized Cryopump Assembly

16"
42cm

12"
30cm

1/4
0.6cm

2"
5cm

FIG. 2

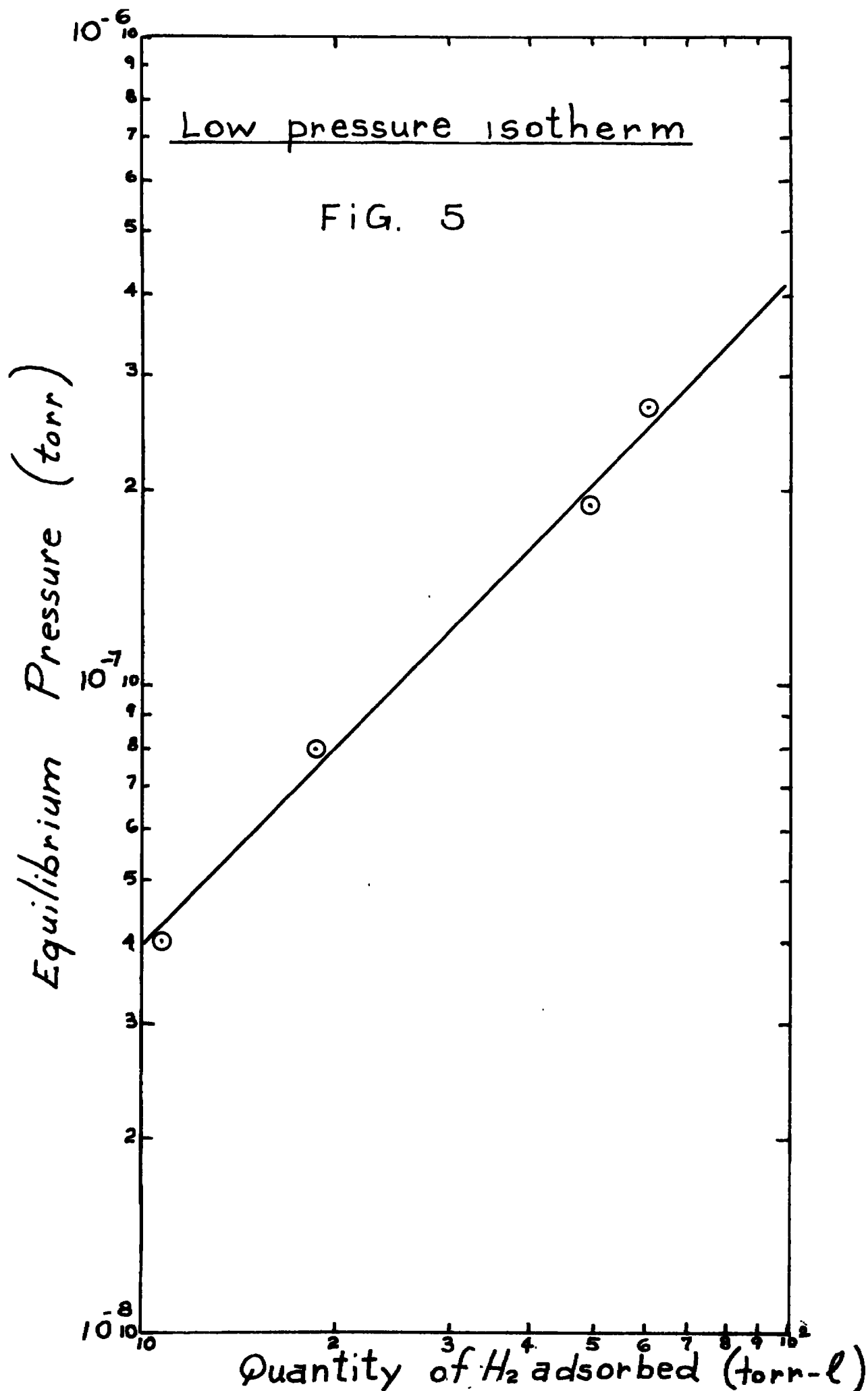Typical H₂ addition sequence

FIG. 3

Adsorption Isotherm
28°K

Equilibrium Pressure (torr)

Quantity of H_2 adsorbed (torr-ℓ)

FiG. 4

Low pressure isotherm

FiG. 5

Equilibrium Pressure (torr)

Quantity of H₂ adsorbed (torr-ℓ)

SPONGE AL   280 X
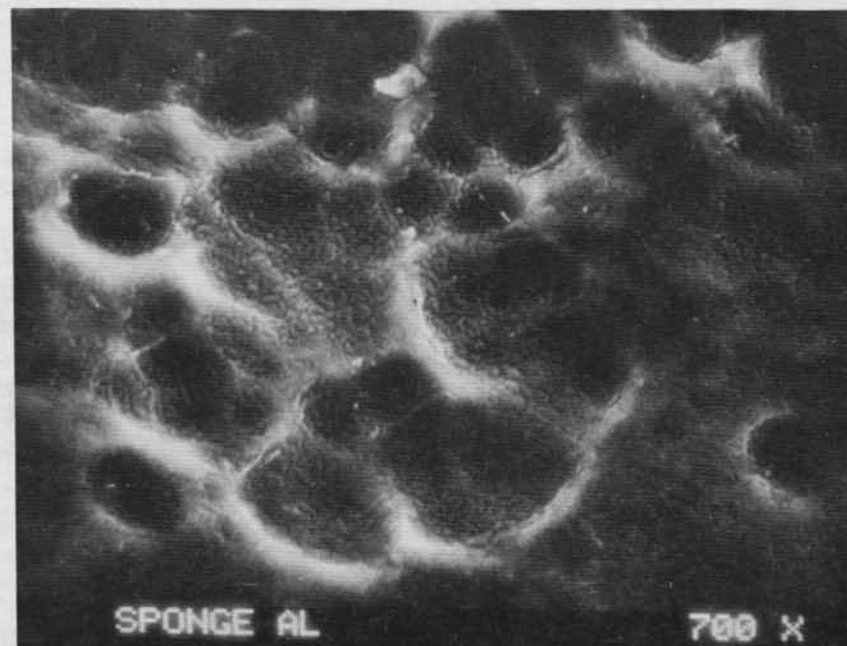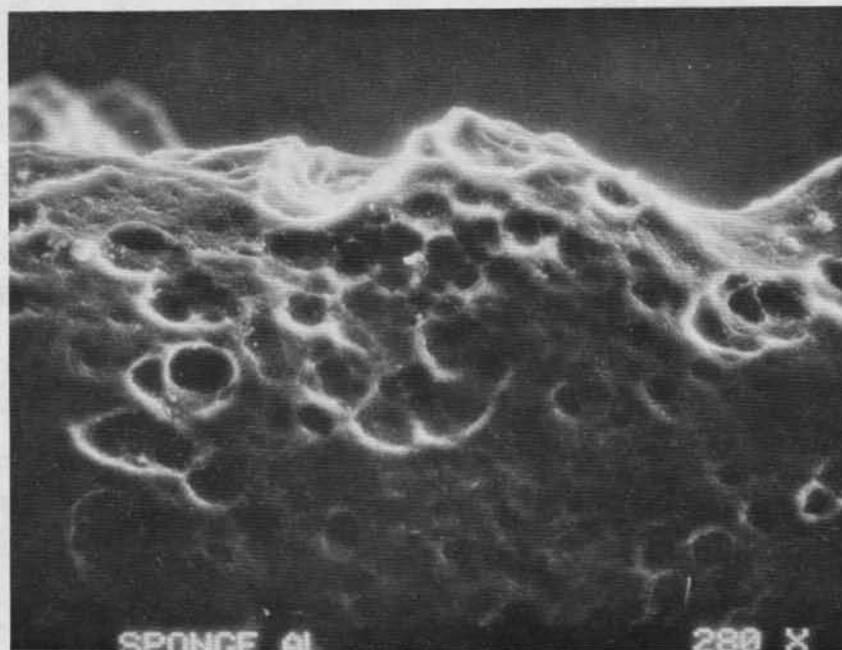
SPONGE AL   700 X

SPONGE AL   2100X
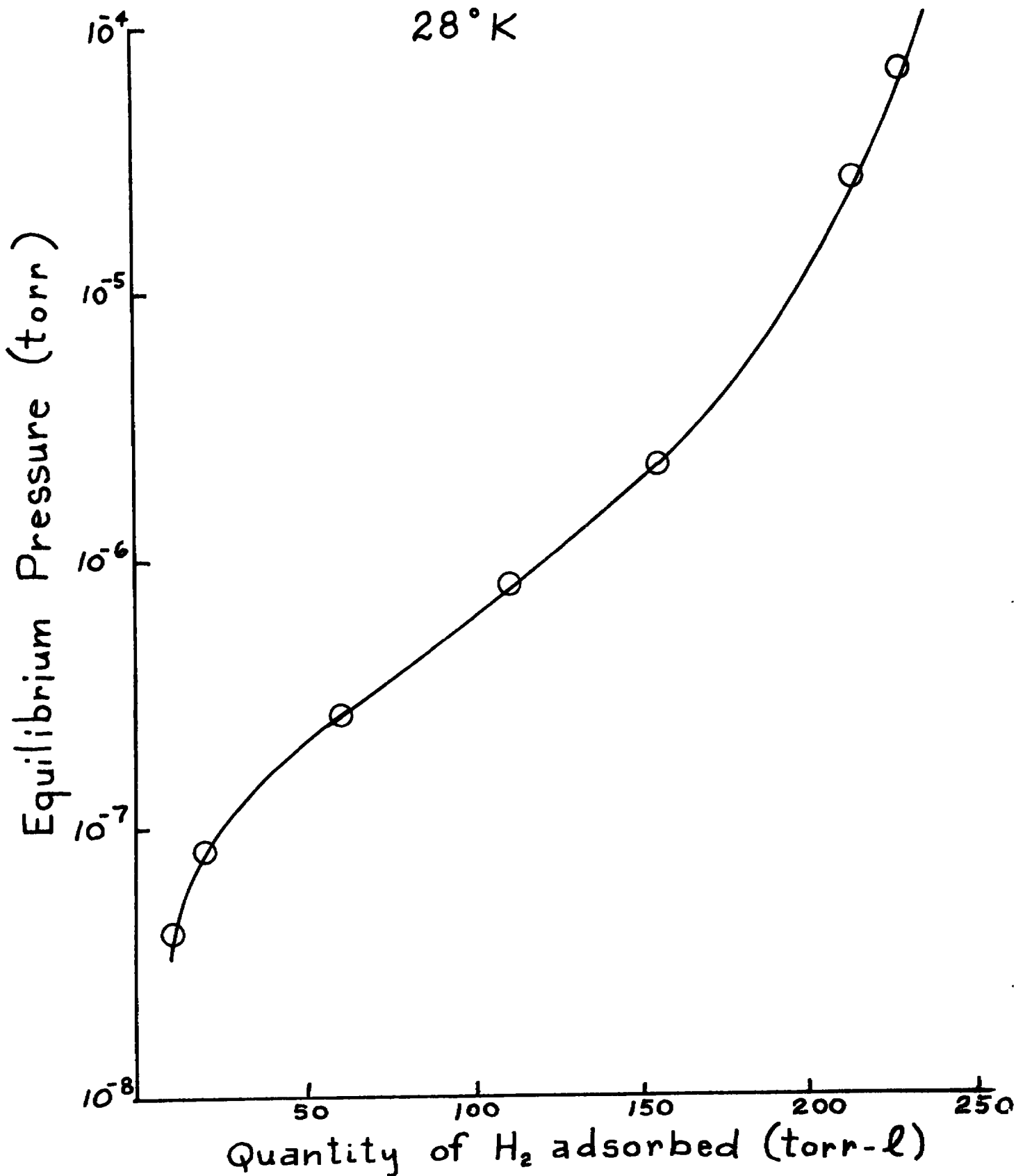
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Fig. 6   Surface of anodic coating